

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Serial No. : 10/822,924 Confirmation No. 3565  
Applicant : Norman D. Hinman  
Filed : April 13, 2004  
TC/Art Unit : 1793  
Examiner : Johnson, Edward M.  
For : COMPOSITION AND METHOD FOR MAKING SILICON-  
CONTAINING PRODUCTS  
Docket No. : 0582429.00001

***Via Electronic Filing***

Mail Stop Amendment  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

**AMENDED DECLARATION OF NORMAN D. HINMAN  
UNDER 37 C.F.R. §1.132**

I, Norman D. Hinman, a co-applicant and named co-inventor of the subject matter disclosed and claimed in the above-referenced patent application, hereby declare as follows:

**BACKGROUND**

1. I hold a Bachelor of Arts degree from Johns Hopkins University (1966), a Ph.D. in Biochemistry from University of Connecticut (1972), and an MS in Chemical Engineering from the Colorado School of Mines (1979). I am a Registered Professional Engineer in the State of Colorado, and have thirty-two publications.

2. I am a Founder and currently the President of Si Options, LLC, the assignee of the subject application and the underlying inventions. Prior to the formation of Si Options, LLC I was employed by BC International (1998-2003); Midwest Research Institute, National Renewable Energy Laboratory (1987-1998); United Engineers (1980-1987); Gates Rubber Company (1979-1980); Eastern Virginia Medical School Department of Biochemistry (1975-1977); and University of Colorado Medical Center, Department of Biophysics (1972-1975).

3. I have read and am generally familiar with U.S. Patent Application No. 10/822,924 (the '924 application), filed April 13, 2004, including the claims that are now pending and under rejection. I consider myself to be a co-inventor of all subject matter claimed in the '924 application. All my interest as a co-inventor in the '924 application and in the claimed invention is assigned to Si Options, LLC.

4. I believe that the field of technology to which the invention pertains to be the conversion of a biomass, specifically rice hulls, into commercially useful, high-purity silicon-containing products.

5. I believe that the skill level of one of ordinary skill in the art includes a graduate degree in chemical engineering or chemistry and not less than about 5 years experience in the area of conversion of biomass into products together with prior experience in the high temperature production of advanced materials.

6. The technology disclosed in the '924 patent application and the inventions recited in the pending claims have not been commercialized but are currently under development by Si Options, LLC ("Si Options"). During the research phase that preceded the development phase, extensive bench-scale contract research work was done under my supervision and under conditions of confidentiality by Hazen Research, Inc. ("Hazen") in Golden, Colorado. Some of the related analytical work was performed by Hazen and other analytical work was performed by Northern Analytical Laboratory, Inc., Merrimack, NH; Wyoming Analytical Laboratories, Inc., Golden, CO; and Particle Technology Labs, Ltd., Downers Grove, IL during the period from August 2003 to

January 2004. The statements made herein are fully supportable by data obtained during the research phase.

## PRODUCTS OF THE INVENTION

### Leach Product

7. Untreated rice hulls contain about 20% silica ( $\text{SiO}_2$ ), about 1-3% (10,000 to 30,000 ppm) non-silica minerals, and from about 77% to 79% organic material by weight. The organic material can be thought of as comprising fixed carbon and volatile carbon. The mole ratio of fixed carbon : silica in untreated rice hulls is about 4:1, and the weight ratio of fixed carbon : volatile carbon is about 5:1.

8. Leaching the rice hulls with an aqueous solution of sulfuric acid produces an intermediate carbon-silica product ("Leach Product"). Leaching (a) reduces the mineral content of the rice hulls significantly; (b) adjusts the mole ratio of fixed carbon : silica in the leached rice hulls; and (c) increases the porosity of the rice hulls.

9. The level of mineral reduction sought depends upon the intended end-use of the Leach Product. If the Leach Product will be used to produce silicon nitride or silicon carbide for advanced ceramic applications, the level of mineral reduction required is moderate. On the other hand, if the Leach Product will be used to produce silicon nitride that will, in turn, be used to produce photovoltaic silicon, the level of mineral reduction sought is very significant. In particular, for use in producing photovoltaic silicon via silicon nitride, it is critical that the levels of phosphorous and boron in the Leach Product be very low.

10. The optimum mole ratio of fixed carbon : silica in the Leach Product also depends on what the Leach Product will be used for. For example, if the product will be used for production of silicon nitride, the optimum mole ratio of fixed carbon : silica is around 2:1. On the other hand, if the Leach Product will be used for production of silicon carbide, the optimum mole ratio of fixed carbon : silica ratio is about 3:1.

11. For all uses it is desirable for the Leach Product to have a high level of porosity as this enhances the rate of reaction during the subsequent carbothermal step used to produce silicon nitride and silicon carbide.

12. The key leaching conditions or parameters that determine the mineral purity, the mole ratio of fixed carbon : silica, and the porosity of the Leach Product are (a) the concentration of rice hulls in the leach mixture; (b) the concentration of sulfuric acid in the leach mixture; (c) the temperature of the leach mixture; and (d) the leach time.

13. Through our investigations, we have discovered that temperature has a significant effect on the mole ratio of fixed carbon : silica in the Leach Product. At the relatively low leach temperature of 25 deg C (room temperature) the fixed carbon: silica ratio of the Leach Product is about 3:1. As the leach temperature increases, the mole ratio declines and reaches a minimum of about 2:1 at about 120 deg C. As the temperature increases, the mole ratio increases and reaches 3:1 at about 160 deg C. At higher temperatures of about 200 deg C and moderate times of about 1 hour, the ratio reaches a high level of about 5:1.

14. Through our investigations, we have also discovered that temperature has a significant effect on the mineral purity of the Leach Product. With regard to mineral purity, Si Options has discovered that close to 99% of the total minerals in the rice hulls can be removed by leaching with sulfuric acid at temperatures of 94 deg C or less. Under these conditions the minerals of sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), and manganese (Mn) can be reduced to levels less than about 10 ppm in the Leach Product. These conditions also greatly reduce the level of phosphorous, but not to the extent that the other minerals are reduced. The level of phosphorous in the Leach Product produced at 94 deg C or less is about 60 ppm. The level of boron is naturally very low in untreated rice hulls, so the level of this element remains low in the Leach Product.

15. We have discovered that almost all of the residual phosphorous remaining after leaching at 94 deg C or less is associated with the surface of the silica particles in rice hulls. The residual phosphorous is “trapped” by a layer of organic material and this layer of organic material can be solubilized by sulfuric acid at a temperature around 120 deg C. Once the organic layer is solubilized, the sulfuric acid can reach the phosphorous bound to the surface of the silica particles and release it. The resulting phosphorous levels in the Leached Product are less than 4 ppm and close to 1 ppm. Thus, increasing the leach temperature above “boiling” is believed to be important to achieving the phosphorous levels needed, for example, for the production of photovoltaic silicon via  $\text{Si}_3\text{N}_4$ .

16. We have also found that the minerals leached out of the rice hulls in each temperature range are released quickly, typically in 30 minutes or less. As a practical matter, 15 minutes is adequate leach time for the production of Leach Product intended for use in the production of silicon-containing products. However, we have determined that significant purification occurs in as little as about 6 seconds of contact with sulfuric acid, which is about the minimum time in which a sample can be pulled after contacting the rice hulls with the acid solution.

17. We have also found that acid concentration and rice hull concentration have some effect on the release of minerals. Acid concentrations greater than 1% and less than 10% provide for the maximum release of minerals. Higher and lower concentrations of acid are not as effective. Rice hull concentration of about 10% provides for maximum release of minerals. Higher and lower rice hull concentrations are not as effective.

#### Devolatilized Leach Product

18. The Leach Product can contain significant volatile carbon. The volatile carbon is carbonaceous material that is volatilized at temperature between about 300 deg C and 1000 deg C under an inert gas atmosphere such as argon. Where it is desirable to separate the release of the volatile carbon from a subsequent carbothermal

reaction, the Leach Product is preferably devolatilized by heating it to a temperature of 900 deg C, to release the volatile carbon. The released volatile carbon is desirably condensed to form an oily byproduct. This devolatilized carbon silica product is referred to as a "Devolatilized Leach Product." The Devolatilized Leach Product should be viewed as an intermediate product that is then desirably fed to a carbothermal reactor. The remaining fixed carbon and silica react to form the silicon-containing product of interest.

19. The carbothermal reactor operates at about 1450 to 2000 deg C. However, the volatile carbon can be removed at a much lower temperature of around 900 deg C. Thus, less energy is used to remove the volatile carbon by carrying out the removal of the volatile carbon at 900 deg C prior to the carbothermal operation instead of at 1450 deg C to 2000 deg C as part of the carbothermal operation.

20. Removal of the volatile carbon in the carbothermal operation may cause the carbothermal reactor to "plug up" due to condensation of the volatile carbon. Removal of the volatile carbon prior to the carbothermal operation avoids this potential problem.

21. Removal of the volatile carbon in the carbothermal operation at about 1450 deg C to 2000 deg C makes the volatile carbon vapors subject to high temperatures which may cause changes in the resulting oil product that make such product less desirable as an energy product or as a feed for chemical production. Removal of the volatile carbon at a lower temperature prior to the carbothermal operation avoids this potential problem.

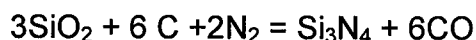
22. If the Leach Product is fed directly to the carbothermal reactor, the volatile carbon is volatilized in the carbothermal reactor while the fixed carbon and silica react to form the silicon-containing product of interest. The volatile carbon will exit the carbothermal reactor in the off-gas stream and can then be condensed to form an oily material that can be used as a fuel or as a chemical feedstock.

23. Although there are some concerns regarding feeding the Leach Product directly to the carbothermal reactor as noted above, directly feeding the Leach Product to the carbothermal reactor means that both the devolatilization and the carbothermal reaction can be carried out in a single operation as opposed to two separate operations. This may reduce capital and operating costs. Whether it is best to carry out devolatilization and the carbothermal reaction in separate reactors or in a single reactor depends on the results of an engineering and economic analysis for a specific commercial plant.

#### Carbothermal Reaction Products (Silicon-Containing Products)

24. In the carbothermal reactor, the fixed carbon removes the oxygens from the silica ( $\text{SiO}_2$ ) to form carbon monoxide and a silicon-containing product. If the desired silicon containing product ("Carbothermal Reaction Product") is silicon carbide, the reactor is operated with an inert gas such as argon. However, if the desired Carbothermal Reaction Product is silicon nitride, the carbothermal reactor is operated under nitrogen.

25. The carbothermal reaction for the production of silicon nitride is as follows:

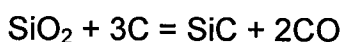


Thus, the stoichiometric carbon : silica mole ratio for the reaction is 2:1 and the feed material to the carbothermal reactor (either the Leach Product or the Devolatilized Leach Product) should have a fixed carbon : silica mole ratio of about 2:1. If the silicon nitride is to be used for producing advanced ceramics, the mineral level in the feed material must be significantly lower than in rice hulls, but not as low as is needed to produce photovoltaic grade silicon. The typical temperature employed for the carbothermal production of silicon nitride is about 1450 deg C.

26. We tested the Leach Product and Devolatilized Leach Product in the carbothermal production of silicon nitride and found conditions where the yield of product is excellent. However, when conventional reactors are used the reaction is very slow, taking as long as 12 hours. Through our investigations, we have discovered that

the rate of production of silicon nitride is extremely sensitive to the concentration of carbon monoxide (CO). Once this was understood, we developed an up-flow carbothermal reactor that keeps the concentration of carbon monoxide very low. As a result, the reaction takes place in less than 1 hour. The up-flow reactor and methods for operating the reactor are also our inventions and are addressed in a separate patent application.

27. The carbothermal reaction for the production of silicon carbide is as follows:



Thus the stoichiometric carbon : silica mole ratio for the reaction is 3:1 and the feed material to the carbothermal reactor (either the Leach Product or the Devolatilized Leach Product) should have a fixed carbon : silica mole ratio of about 3:1. If the silicon carbide is to be used for producing advanced ceramics, the mineral level in the feed material must be significantly lower than in rice hulls, but not as low as is needed to product photovoltaic grade silicon. The typical temperature employed for the carbothermal production of beta- silicon carbide is about 1500 deg C and the typical temperature employed for the carbothermal production of alpha- silicon carbide is about 2,000 deg C.

28. We tested the Leach Product and Devolatilized Leach Product in the carbothermal production of silicon carbide and found that the reaction proceeds much faster than is seen with the commercial silicon carbide production process. Moreover the yield of product is much better than is attained with the commercial process. Moreover, we discovered that if the carbon : silica mole ratio of the feed material is somewhat less than 2:1, the alpha- silicon carbide product is free of any residual carbon or silica and is extremely pure with regard to mineral contamination.

#### Oxidized Silicon Carbide Product

29. We found that if the feed material to the carbothermal reaction for the production of silicon carbide is somewhat silica rich, i.e., the carbon : silica mole ratio is



somewhat less than 3:1, the resulting alpha-silicon carbide product is clean, i.e., does not contain any residual carbon or silica. However, the beta-silicon carbide contains some residual silica. On the other hand, if the feed material contains a fixed carbon : silica mole ratio somewhat greater than 3:1, the silicon carbide product (alpha- or beta-) will contain some residual carbon. This residual carbon must be reduced. In this regard, we developed an oxidation step that removes the residual carbon from the silicon carbide product of the carbothermal step without oxidizing the silicon carbide. Air is used as the oxidizing agent and the temperature of about 1,000 degrees is satisfactory for this purpose.

#### Oxidized Silicon Nitride Product

30. We found that the best yields of silicon nitride are obtained from a feed material (either the Leach Product or the Devolatilized Leach Product) that is carbon rich, i.e. a feed that contains a fixed carbon : silica mole ratio of greater than 2:1. However, the silicon nitride product contains both residual carbon and some residual silica. Both of these materials must be reduced. In this regard, we developed an oxidation step that removes residual carbon from the silicon nitride product of the carbothermal step without oxidizing the silicon nitride. Air is used as the oxidizing agent and the optimum temperature is about 1000 deg C. With temperatures of about 1200 deg C and greater, silicon nitride is partially oxidized to silica. The oxidation of silicon nitride reduces the product yield, which can have a negative impact on revenue and, therefore, a direct negative impact on profitability.

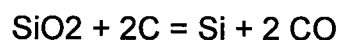
#### Sodium Hydroxide-Treated Silicon Carbide and Silicon Nitride Products

31. In addition, we developed a unique process that involves the use of sodium hydroxide to dissolve the residual silica from both beta-silicon carbide and silicon nitride. We also discovered that sodium hydroxide treatment removes any residual phosphorous from the silicon nitride product. This is particularly important if the silicon nitride is to be used to produce photovoltaic grade silicon. We have discovered that favorable results are achieved when the sodium hydroxide solution has a

concentration of about 4% and the treatment takes place at about 92 deg C.

### Dissociated Silicon Product

32. Originally, we intended to produce silicon according to the following well know carbothermal reaction:



Our thermodynamic analysis of this reaction indicated that the reaction would proceed under argon at a temperature of about 2,000 deg C. However, the analysis also showed that at a temperature of about 1,500 deg C, silicon carbide would form. Thus, the feed material must be heated to 2,000 deg C very quickly. If it is heated slowly, silicon carbide will form at the lower temperature before the silicon can form. We carried out several tests with furnaces that had reasonably fast heat-up rates in an attempt to get past the temperature of about 1500 deg C as quickly as possible. However, we were not successful in getting past this temperature quickly enough to avoid the formation of silicon carbide.

33. We performed additional thermodynamic modeling indicating that at around 1750 deg C, silicon nitride dissociates to molten silicon and gaseous nitrogen. We subsequently tested this idea with commercial silicon nitride using a conventional reactor and found that the silicon nitride could be completely dissociated to nitrogen and silicon and that the nitrogen could be removed in the off-gas stream, leaving the molten silicon. Next we tested this idea with our own silicon nitride product made from rice hulls in a conventional reactor and got the same results. We have found that the oxidized and sodium hydroxide-treated silicon nitride product can be dissociated into extremely pure silicon and nitrogen. The dissociated silicon is suitable, for example, for use in the production of solar panels. The idea of using silicon nitride from rice hulls to produce photovoltaic silicon is addressed in a separate patent application.

34. As it turns out, the method of paragraph 33 is actually preferred over the typical carbothermal route. This is because the production of silicon nitride with an up-flow reactor and the subsequent dissociation of silicon nitride to silicon and nitrogen are,

together, much faster than the traditional carbothermal process for the production of silicon, which typically takes a day or longer, and a subsequent process to purify the carbothermal silicon. This is also because the last bits of residual phosphorous can be removed from the silicon nitride product by treatment with sodium hydroxide. Thus, because the resulting silicon nitride is extremely pure, having very low levels of phosphorous, the silicon from disassociation of silicon nitride is extremely pure. On the other hand, if the silicon was produced directly in a carbothermal step, the residual phosphorus would become trapped in the molten silicon and after solidification of the silicon, it would be impossible to remove this small amount of residual phosphorous

#### PRIOR ART

35. I have read and am generally familiar with the Office Action mailed October 30, 2008 that rejects claims 106-160 of the '924 application under 35 U.S.C. §103(a) as being unpatentable over U.S. 4,591,492 to Tanaka, et al. ("Tanaka") and, independently, as being unpatentable over U.S. 6,117,810 to Lee et al. ("Lee"). I have also read and am generally familiar with the Tanaka and Lee patents. For reasons stated below, I respectfully disagree with Examiner's conclusions regarding the alleged obviousness of my claimed inventions.

#### U.S. 4,591,492 to Tanaka, et al.

##### A. Products of Interest.

36. Tanaka only discloses a method for making silicon carbide, although Tanaka mentions that U.S. 4,525,335 illustrates the formation of silicon nitride whisker crystals (Col. 11, lines 32-45). In contrast, the subject application claims (1) carbon-silica products (above, "Leached Product"); (2) devolatilized carbon-silica products (above, "Devolatilized Leach Product"); (3) silicon carbide; (4) silicon nitride and (5) silicon.

37. Tanaka makes no composition of matter claims on silicon carbide or any

other intermediate products such as the product of the leaching operation. Moreover, Tanaka fails to disclose the effect of leaching on the carbon-silica mole ratios of the leach product or any other products. In contrast, we make composition of matter claims on all of the above mentioned products and disclose detailed information on the effects of the leaching operation on the carbon : silica mole ratio of the leach products.

38. Although Tanaka mentions the carbon : silicon ratio of the rice hulls used, it makes no mention of the carbon : silicon ratios of the leach product or any other intermediate product. The carbon : silicon ratios stated in Tanaka for the rice hulls are from "7:3 to 5:5" (Column 3). These are the same as 2.33:1 and 1:1. The Tanaka values are not even close to the value of about 4:1 that is consistently given in the literature. Thus, Tanaka's ability to measure even the carbon : silica mole ratio of the rice hulls is called into question. Moreover, these ratios are well below the desired ratio of about 3:1 for silicon carbide production and it is hard to imagine how his leaching process could increase the ratio from the low values he gives for rice hulls to higher values in the leached product.

39. It is not obvious from Tanaka what the effect of hydrochloric acid is on the carbon : silica mole ratio in the leach product, let alone what the effect of sulfuric acid would have on the carbon : silica mole ratio in the leach product or any other intermediate product.

#### B. Type of acid.

40. Tanaka discloses the use of hydrochloric acid, nitric acid and sulfuric acid. In contrast, to the extent that our claims recite an acid, they recite only sulfuric acid.

41. The information and discussion in Tanaka are focused on hydrochloric acid. Tanaka contains no evidence about the use or affects of acids other than hydrochloric acid with or on rice hulls. Tanaka does not provide any rationale or teaching for why other acids might provide desired results. It is well know that different

acids have different effects on biomass and there is no reason to expect, *a priori*, that the results achieved with one acid such as hydrochloric acid will be duplicated or even close with another acid. For example, cellulose is a major component of rice hulls and it is well known that sulfuric acid hydrolyzes cellulose to the individual glucose molecules that make up cellulose. On the other hand, nitric acid is an oxidizing agent and its effect on cellulose and other components of biomass is different from that of sulfuric acid.

42. It is therefore not obvious from Tanaka what the effects of sulfuric acid will be on rice hulls.

#### C. Acid Concentration.

43. Tanaka discloses a method of manufacturing silicon carbide crystals in which a rice husk raw material is treated with an acid solution (e.g. 5N to 6 N  $\text{H}_2\text{SO}_4$ , or HCl or  $\text{HNO}_3$ ) prior to being heated in a furnace of non-oxidizing atmosphere. Tanaka expresses the recommended acid concentrations in terms of normality—5-6 N. In the text, Tanaka also states that concentrated HCl is 12 normal, but it doesn't tell the reader that 12 normal HCl is actually only 37 % HCl. Thus, the reader has to know what the actual concentration of 12 N HCl is before he can determine the actual wt % of HCl in the leach solution. By assuming that concentrated HCl is 37% HCl, we calculate the HCl concentrations of 5-6 N solutions to be 15% to 19% HCl, which, to us, seems like a high concentration of HCl.

44. Turning now to sulfuric acid, Tanaka presents no evidence regarding the effect of sulfuric acid on rice hulls, but suggests that the same concentrations of acid used for HCl (5-6N) will work optimally for  $\text{H}_2\text{SO}_4$ . Tanaka states that concentrated sulfuric acid is 36 N, and the reader must know that such acid contains 98% sulfuric acid, and then carry out a calculation to try to figure out the actual concentration of sulfuric acid to which Tanaka is referring. We calculate that 5-6 N  $\text{H}_2\text{SO}_4$  corresponds to an acid concentration of 14-16 wt %. This is a very high acid concentration that is well above the optimum concentration (1-2.5wt %) recommended in our application. In this regard, we have evidence that sulfuric acid concentrations above about 5% results in

leach products that contain significantly more phosphorous.

45. Tanaka fails to teach the importance of acid concentration and does not disclose the use of sulfuric acid concentrations as claimed in our application. Moreover, Tanaka teaches that excessive dilution of the acid with water will lessen its effectiveness.

46. We also have evidence indicating that sulfuric acid, at the concentrations of hydrochloric acid used by Tanaka, provides less than desirable results. It is not obvious from Tanaka what affects lower, more cost- effective concentrations of hydrochloric acid will have on the leach product and it is certainly not obvious from Tanaka what effects the concentration of sulfuric acid claimed will have on the leach product.

#### D. Rice Hull Concentration.

47. At Column 3, Tanaka states that the amount of acid utilized in the pretreatment step is preferably 10 to 40 liters per kilogram of rice husks (approximately 10 to 40 weight percent, based on the weight of the husks), optimally 20-30 liters/Kg. (approximately to 30 percent). Tanaka says the 20 to 30 liter range is particularly appropriate in instances where the mixture of rice husks is agitated during the treatment process.

48. A liter of acid weighs about 1 Kg. Thus, 10 liters of acid mixed with 1 Kg of rice husks produces a slurry that is about 10 wt% rice husks. However 40 liters of acid mixed with 1 Kg of rice husks results in a slurry that is about 3% rice husks as opposed to the 40% indicated by Tanaka. Thus, Tanaka provides information that is inconsistent and confusing with regard to the rice hull concentration he actually used, and the reader does not know what rice hull concentrations he actually used.

49. Tanaka fails to disclose teachings regarding what the desirable concentration of rice hulls is in the leaching process with sulfuric acid. In contrast, we

clearly describe the actual rice hull concentration used in all examples of the leaching process and in discussions of the leaching process.

#### E. Temperature.

50. Tanaka discloses "boiling". However, the temperature of "boiling" is highly dependent on the location and on the type and concentration of acid. Thus the actual temperature that Tanaka discloses is unknown. In contrast, we disclose a range of leaching temperatures from 10 deg C to 250 deg C and provide detailed information on the different effects of different temperatures.

51. It is not obvious from Tanaka how temperature affects the properties of the leach product produced with hydrochloric acid, and it is certainly not obvious from Tanaka what effect the leaching temperature would have on the properties and purity of the Leach Product produced with sulfuric acid.

52. In Column 3, Tanaka states that although the application of heat or agitation will lessen the pretreatment time, boiling is most effective. Use of the word "boiling" does not tell the reader what the temperature actually was. The boiling point of a solution of HCl is highly dependent upon the concentration of HCl, the altitude where the treatment takes place and the concentration of rice hulls. At sea level, a 10% solution of HCl boils at about 103 deg C, whereas a 20% solution of HCl boils at 108 deg C, whereas a 38% solution of HCl boils at 48 deg C. If Tanaka's HCl solutions are 5-6 N, the boiling point at sea level is about 103 deg C to 108 deg C. However, even with some knowledge of the effect of the concentration of HCL on the boiling point of HCL solution at sea level, one does not know Tanaka's actual temperature.

53. We have found that relatively small changes in temperatures between "boiling" and 120 deg C can have a significant effect on the concentration of elements such as phosphorus and iron in the leached product. Because this biomass system and process involve both organic and inorganic components, significant changes can and do occur during acid leaching that likely would not be apparent to one accustomed to

working primarily with organic components.

54. Tanaka's imprecise definition of temperature does not allow the reader to make any real correlation between the actual temperature and the effects described by Tanaka. Furthermore, the boiling point of water at sea level is about 100 deg C, but in Golden, Colorado where we have done our work, the boiling point of water is about 96 deg C. Thus without telling the reader the altitude connected to his "boiling point," one is even more confused about what the actual temperature was.

F. Time.

55. Tanaka discloses boiling for a period of 0.5 hours to one hour, or preferably 2 hours (Col. 13, lines 1-3). In contrast, we disclose and recite in our claims a range of times from six seconds to 48 hours, and provide descriptions of the effects of different leaching times. It is not obvious from Tanaka how different leaching times affect the leach product of the hydrochloric leach operation. No trends are shown. Thus one would be forced to carry out a complete analysis of the effect of time on the product of the leach process even if hydrochloric acid were used. Clearly, with respect to the use of sulfuric acid, it is not obvious from Tanaka what the effect of time has on the leach product.

U.S. 6,117,810 to Lee, et al.

56. I believe Lee is unrelated to the subject application. The products are not the same. The raw materials are not the same. The processes for converting the raw material into the product are completely different.

57. The product of interest in Lee is a molecular sieve compound made of carbon and aluminosilicate. The products of interest in our application are (1) carbon-silica products (above, "Leached Product"); (2) devolatilized carbon-silica products (above, "Devolatilized Leach Product"); (3) silicon carbide; (4) silicon nitride and (5) silicon.



58. The raw materials used in Lee are activated carbon, various aluminum containing materials, and colloidal silica or fumed silica or water glass or silica gel. The raw materials used in our application are rice hulls, rice straw and other plant materials containing at least 1% silica.

59. The Lee process involves forming an aluminum silicate gel and then embedding the gel in the pores of the activated carbon. The leaching step of our process involves treating rice hulls, rice straw and other plant matter containing at least 1% silica with various concentrations of sulfuric acid at various temperatures and for various times to produce carbon silica products with mineral concentrations much lower than the concentrations in rice hulls, and with carbon : silica mole ratios optimal for the production of the Devolatilized Leach Product, silicon, silicon carbide, silicon nitride and silicon tetrachloride, and with much higher porosity than rice hulls.

60. All testing referred to in paragraphs 7-8, 12-17 and part of the testing mentioned in paragraph 18 above were done prior to filing the subject application. Part of the testing mentioned in paragraph 18 above and all of the testing referred to in paragraphs 19, 22 and 24-34 were done after the filing of the subject application.

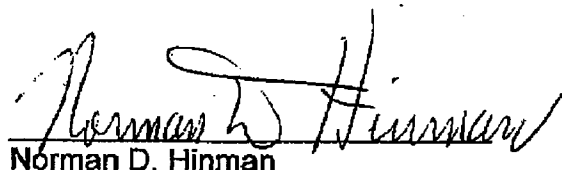
61. I believe that an invention embodying the elements recited in combination in each respective pending claim as amended in the Amendment and Response filed concurrently with this Declaration have not been disclosed in any prior art reference of which I am aware. I further believe that the invention as recited in each claim presented in the application as amended in the Response filed concurrently with this Declaration would not have been obvious to a person of ordinary skill in the art having knowledge of the prior art at the time my disclosures of the claimed subject matter were made in the '924 application.

62. All statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true. To the extent that any statement made herein differs, or can be read or interpreted to differ, from any

Declaration of Norman D. Hinman  
Application No. 10/822,924

statement made in my Declaration previously made in connection with the prosecution of United States Patent Application No. 10/822,924 on April 29, 2009 ("Prior Declaration"), any and all such differences are based upon more careful reading of the Prior Declaration and/or the cited prior art references and/or error inadvertently made during preparation of the Prior Declaration, all of which were made in good faith and without any intent to deceive the Examiner, the United States Patent and Trademark Office, or any other person who may later have reason to read or consider my statements made in the Prior Declaration or herein.

I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. §1001), and may jeopardize the validity of the application or any patent issuing thereon.



Norman D. Hinman

Date: July 1, 2009

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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Docket No. : 0582429.00001

***Via Electronic Filing***

**FOR EXAMINER'S USE**

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Dear Sir:

**AMENDED DECLARATION OF NORMAN D. HINMAN  
UNDER 37 C.F.R. §1.132**

I, Norman D. Hinman, a co-applicant and named co-inventor of the subject matter disclosed and claimed in the above-referenced patent application, hereby declare as follows:

**BACKGROUND**

1. I hold a Bachelor of Arts degree from Johns Hopkins University (1966), a Ph.D. in Biochemistry from University of Connecticut (1972), and an MS in Chemical Engineering from the Colorado School of Mines (1979). I am a Registered Professional Engineer in the State of Colorado, and have thirty-two publications.

2. I am a Founder and currently the President of Si Options, LLC, the assignee of the subject application and the underlying inventions. Prior to the formation of Si Options, LLC I was employed by BC International (1998-2003); Midwest Research Institute, National Renewable Energy Laboratory (1987-1998); United Engineers (1980-1987); Gates Rubber Company (1979-1980); Eastern Virginia Medical School Department of Biochemistry (1975-1977); and University of Colorado Medical Center, Department of Biophysics (1972-1975).

3. I have read and am generally familiar with U.S. Patent Application No. 10/822,924 (the '924 application), filed April 13, 2004, including the claims that are now pending and under rejection. I consider myself to be a co-inventor of all subject matter claimed in the '924 application. All my interest as a co-inventor in the '924 application and in the claimed invention is assigned to Si Options, LLC.

4. I believe that the field of technology to which the invention pertains to be the conversion of a biomass, specifically rice hulls, into commercially useful, high-purity silicon-containing products.

5. I believe that the skill level of one of ordinary skill in the art includes a graduate degree in chemical engineering or chemistry and not less than about 5 years experience in the area of conversion of biomass into products together with prior experience in the high temperature production of advanced materials.

6. The technology disclosed in the '924 patent application and the inventions recited in the pending claims have not been commercialized but are currently under development by Si Options, LLC ("Si Options"). During the research phase that preceded the development phase, extensive bench-scale contract research work was done under my supervision and under conditions of confidentiality by Hazen Research, Inc. ("Hazen") in Golden, Colorado. Some of the related analytical work was performed by Hazen and other analytical work was performed by Northern Analytical Laboratory, Inc., Merrimack, NH; Wyoming Analytical Laboratories, Inc., Golden, CO; and Particle Technology Labs, Ltd., Downers Grove, IL during the period from August 2003 to

January 2004. The statements made herein are fully supportable by data obtained during the research phase.

## PRODUCTS OF THE INVENTION

### Leach Product

7. Untreated rice hulls contain about 20% silica ( $\text{SiO}_2$ ), about 1-3% (10,000 to 30,000 ppm) non-silica minerals, and from about 77% to 79% organic material by weight. The organic material can be thought of as comprising fixed carbon and volatile carbon. The mole ratio of fixed carbon : silica in untreated rice hulls is about 4:1, and the weight ratio of fixed carbon : volatile carbon is about 5:1.

8. Leaching the rice hulls with an aqueous solution of sulfuric acid produces an intermediate carbon-silica product ("Leach Product"). Leaching (a) reduces the mineral content of the rice hulls significantly; (b) adjusts the mole ratio of fixed carbon : silica in the leached rice hulls; and (c) increases the porosity of the rice hulls.

9. The level of mineral reduction sought depends upon the intended end-use of the Leach Product. If the Leach Product will be used to produce silicon nitride or silicon carbide for advanced ceramic applications, the level of mineral reduction required is moderate. On the other hand, if the Leach Product will be used to produce silicon nitride that will, in turn, be used to produce photovoltaic silicon, the level of mineral reduction sought is very significant. In particular, for use in producing photovoltaic silicon via silicon nitride, it is critical that the levels of phosphorous and boron in the ~~leach product~~ Leach Product be very low.

10. The optimum mole ratio of fixed carbon : silica in the Leach Product also depends on what the Leach Product will be used for. For example, if the product will be used for production of silicon nitride, the optimum mole ratio of fixed carbon : silica is around 2:1. On the other hand, if the Leach Product will be used for production of silicon carbide, the optimum mole ratio of fixed carbon : silica ratio is about 3:1.

11. For all uses it is desirable for the Leach Product to have a high level of porosity as this enhances the rate of reaction during the subsequent carbothermal step used to produce silicon nitride and silicon carbide.

12. The key leaching conditions or parameters that determine the mineral purity, the mole ratio of fixed carbon : silica, and the porosity of the Leach Product are (a) the concentration of rice hulls in the leach mixture; (b) the concentration of sulfuric acid in the leach mixture; (c) the temperature of the leach mixture; and (d) the leach time.

13. Through our investigations, we have discovered that temperature has a significant effect on the mole ratio of fixed carbon : silica in the Leach Product. At the relatively low leach temperature of 25 deg C (room temperature) the fixed carbon: silica ratio of the Leach Product is about 3:1. As the leach temperature increases, the mole ratio declines and reaches a minimum of about 2:1 at about 120 deg C. As the temperature increases, the mole ratio increases and reaches 3:1 at about 160 deg C. At higher temperatures of about 200 deg C and moderate times of about 1 hour, the ratio reaches a high level of about 5:1.

14. Through our investigations, we have also discovered that temperature has a significant effect on the mineral purity of the Leach Product. With regard to mineral purity, Si Options has discovered that close to 99% of the total minerals in the Leach Product rice hulls can be removed by leaching with sulfuric acid at temperatures of 94 deg C or less. Under these conditions the minerals of sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), and manganese (Mn) can be reduced to levels less than about 10 ppm in the Leach Product. These conditions also greatly reduce the level of phosphorous, but not to the extent that the other minerals are reduced. The level of phosphorous in the Leach Product produced at 94 deg C or less is about 60 ppm. The level of boron is naturally very low in untreated rice hulls, so the level of this element remains low in the Leach Product.

15. ~~Almost~~We have discovered that almost all of the residual phosphorous remaining after leaching at 94 deg C or less is associated with the surface of the silica particles in rice hulls. The residual phosphorous is “trapped” by a layer of organic material and this layer of organic material can be solubilized by sulfuric acid at a temperature around 120 deg C. Once the organic layer is solubilized, the sulfuric acid can reach the phosphorous bound to the surface of the silica particles and release it. The resulting phosphorous levels in the Leached Product are less than 4 ppm and close to 1 ppm. Thus, increasing the leach temperature above “boiling” is believed to be important to achieving the phosphorous levels needed, for example, for the production of photovoltaic silicon via  $\text{Si}_3\text{N}_4$ .

16. We have also found that the minerals leached out of the rice hulls in each temperature range are released quickly, typically in 30 minutes or less. As a practical matter, 15 minutes is adequate leach time for the production of Leach Product intended for use in the production of silicon-containing products. However, we have determined that significant purification occurs in as little as about 6 seconds of contact with sulfuric acid, which is about the minimum time in which a sample can be pulled after contacting the rice hulls with the acid solution.

17. We have also found that acid concentration and rice hull concentration have some effect on the release of minerals. Acid concentrations greater than 1% and less than 10% provide for the maximum release of minerals. Higher and lower concentrations of acid are not as effective. Rice hull concentration of about 10% provides for maximum release of minerals. Higher and lower rice hull concentrations are not as effective.

#### Devolatilized Leach Product

18. The Leach Product can contain significant volatile carbon. The volatile carbon is carbonaceous material that is volatilized at temperature between about 300 deg C and 1000 deg C under an inert gas atmosphere such as argon. Where it is desirable to separate the release of the volatile carbon from a subsequent carbothermal

reaction, the Leach Product is preferably devolatilized by heating it to a temperature of 900 deg C, to release the volatile carbon. The released volatile carbon is desirably condensed to form an oily byproduct. This devolatilized carbon silica product is referred to as a "Devolatilized Leach Product." The Devolatilized Leach Product should be viewed as an intermediate product that is then desirably fed to a carbothermal reactor. The remaining fixed carbon and silica react to form the silicon-containing product of interest.

19. The carbothermal reactor operates at about 1450 to 2000 deg C. However, the volatile carbon can be removed at a much lower temperature of around 900 deg C. Thus, less energy is used to remove the volatile carbon by carrying out the removal of the volatile carbon at 900 deg C prior to the carbothermal operation instead of at 1450 deg C to 2000 deg C as part of the carbothermal operation.

20. Removal of the volatile carbon in the carbothermal operation may cause the carbothermal reactor to "plug up" due to condensation of the volatile carbon. Removal of the volatile carbon prior to the carbothermal operation avoids this potential problem.

21. Removal of the volatile carbon in the carbothermal operation at about 1450 deg C to 2000 deg C makes the volatile carbon vapors subject to high temperatures which may cause changes in the resulting oil product that make such product less desirable as an energy product or as a feed for chemical production. Removal of the volatile carbon at a lower temperature prior to the carbothermal operation avoids this potential problem.

22. If the Leach Product is fed directly to the carbothermal reactor, the volatile carbon is volatilized in the carbothermal reactor while the fixed carbon and silica react to form the silicon-containing product of interest. The volatile carbon will exit the carbothermal reactor in the off-gas stream and can then be condensed to form an oily material that can be used as a fuel or as a chemical feedstock.



23. Although there are some concerns regarding feeding the Leach Product directly to the carbothermal reactor as noted above, directly feeding the Leach Product to the carbothermal reactor means that both the devolatilization and the carbothermal reaction can be carried out in a single operation as opposed to two separate operations. This may reduce capital and operating costs. Whether it is best to carry out these steps devolatilization and the carbothermal reaction in separate reactors or in a single reactor depends on the results of an engineering and economic analysis for a specific commercial plant.

#### Carbothermal Reaction Product Products (Silicon-Containing Products)

24. In the carbothermal reactor, the fixed carbon removes the oxygens from the silica ( $\text{SiO}_2$ ) to form carbon monoxide and a silicon-containing product. If the desired silicon containing product ("Carbothermal Reaction Product") is silicon carbide, the reactor is operated with an inert gas such as argon. However, if the desired Carbothermal Reaction Product is silicon nitride, the carbothermal reactor is operated under nitrogen.

25. The carbothermal reaction for the production of silicon nitride is as follows:

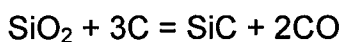


Thus, the stoichiometric carbon : silica mole ratio for the reaction is 2:1 and the feed material to the carbothermal reactor (either the Leach Product or the Devolatilized Leach Product) should have a fixed carbon : silica mole ratio of about 2:1. If the silicon nitride is to be used for producing advanced ceramics, the mineral level in the feed material must be significantly lower than in rice hulls, but not as low as is needed to produce photovoltaic grade silicon. The typical temperature employed for the carbothermal production of silicon nitride is about 1450 deg C.

26. We tested the Leach Product and Devolatilized Leach Product in the carbothermal production of silicon nitride and found that conditions where the yield of product is excellent. However, when conventional reactors are used the reaction is very slow, taking as long as 12 hours. Through our investigations, we have discovered that

the rate of production of silicon nitride is extremely sensitive to the concentration of carbon monoxide (CO). Once this was understood, we developed an up-flow carbothermal reactor that keeps the concentration of carbon monoxide very low. As a result, the reaction takes place in less than 1 hour. The up-flow reactor and methods for operating the reactor are also our inventions and are addressed in a separate patent application.

27. The carbothermal reaction for the production of silicon carbide is as follows:



Thus the stoichiometric carbon : silica mole ratio for the reaction is 3:1 and the feed material to the carbothermal reactor (either the Leach Product or the Devolatilized Leach Product) should have a fixed carbon : silica mole ratio of about 3:1. If the silicon carbide is to be used for producing advanced ceramics, the mineral level in the feed material must be significantly lower than in rice hulls, but not as low as is needed to product photovoltaic grade silicon. The typical temperature employed for the carbothermal production of beta- silicon carbide is about 1500 deg C and the typical temperature employed for the carbothermal production of alpha- silicon carbide is about 2,000 deg C.

28. We tested the Leach Product and Devolatilized Leach Product in the carbothermal production of silicon carbide and found that the reaction proceeds much faster than is seen with the commercial silicon carbide production process. Moreover the yield of product is much better than is attained with the commercial process. Moreover, we discovered that if the carbon : silica mole ratio of the feed material is somewhat less than 2:1, the alpha- silicon carbide product is free of any residual carbon or silica and is extremely pure with regard to mineral contamination.

#### Oxidized Silicon Carbide Product

29. We found that if the feed material to the carbothermal reaction for the production of silicon carbide is somewhat silica rich, i.e., the carbon : silica mole ratio is

somewhat less than 3:1, the resulting alpha-silicon carbide product is clean, i.e., does not contain any residual carbon or silica. However, the beta-silicon carbide contains some residual silica. On the other hand, if the feed material contains a fixed carbon : silica mole ratio somewhat greater than 3:1, the silicon carbide product (alpha- or beta-) will contain some residual carbon. This residual carbon must be reduced. In this regard, we developed an oxidation step that removes the residual carbon from the silicon carbide product of the carbothermal step without oxidizing the silicon carbide. Air is used as the oxidizing agent and the temperature of about 1,000 degrees is satisfactory for this purpose.

#### Oxidized Silicon Nitride Product

30. We found that the best yields of silicon nitride are obtained from a feed material (either the Leach Product or the Devolatilized Leach Product) that is carbon rich, i.e. a feed that contains a fixed carbon : silica mole ratio of greater than 2:1. However, the silicon nitride product contains both residual carbon and some residual silica. Both of these materials must be reduced. In this regard, we developed an oxidation step that removes residual carbon from the silicon nitride product of the carbothermal step without oxidizing the silicon nitride. Air is used as the oxidizing agent and the optimum temperature is about 1000 deg C. With temperatures of about 1200 deg C and greater, silicon nitride is partially oxidized to silica. The oxidation of silicon nitride reduces the product yield, which can have a negative impact on revenue and, therefore, a direct negative impact on profitability.

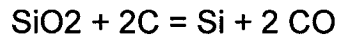
#### Sodium Hydroxide-Treated Silicon Carbide and Silicon Nitride Products

31. In addition, we developed a unique process that involves the use of sodium hydroxide to dissolve the residual silica from both beta-silicon carbide and silicon nitride. We also discovered that sodium hydroxide treatment removes any residual phosphorous from the silicon nitride product. This is particularly important if the silicon nitride is to be used to produce photovoltaic grade silicon. We have discovered

that favorable results are achieved when the sodium hydroxide solution has a concentration of about 4% and the treatment takes place at about 92 deg C.

### Dissociated Silicon Product

32. ~~We have found that the oxidized and sodium hydroxide-treated silicon nitride product can be dissociated into extremely pure silicon and nitrogen. The dissociated silicon is suitable, for example, for use in the production of solar panels. Originally, we intended to produce silicon according to the following well know carbothermal reaction:~~



Our thermodynamic analysis of this reaction indicated that the reaction would proceed under argon at a temperature of about 2,000 deg C. However, the analysis also showed that at a temperature of about 1,500 deg C, silicon carbide would form. Thus, the feed material must be heated to 2,000 deg C very quickly. If it is heated slowly, silicon carbide will form at the lower temperature before the silicon can form. We carried out several tests with furnaces that had reasonably fast heat-up rates in an attempt to get past the temperature of about 1500 deg C as quickly as possible. However, we were not successful in getting past this temperature quickly enough to avoid the formation of silicon carbide.

33. We performed additional thermodynamic modeling indicating that at around 1750 deg C, silicon nitride dissociates to molten silicon and gaseous nitrogen. We subsequently tested this idea with commercial silicon nitride using a conventional reactor and found that the silicon nitride could be completely dissociated to nitrogen and silicon and that the nitrogen could be removed in the off-gas stream, leaving the molten silicon. Next we tested this idea with our own silicon ~~nitride~~nitride product made from rice hulls in a conventional reactor and got the same results. We have found that the oxidized and sodium hydroxide-treated silicon nitride product can be dissociated into extremely pure silicon and nitrogen. The dissociated silicon is suitable, for example, for use in the production of solar panels. The idea of using silicon nitride from rice hulls to produce photovoltaic silicon is addressed in a separate patent application.

34. As it turns out, the method of paragraph 33 is actually preferred over the typical carbothermal route. This is because the production of silicon nitride with an up-flow reactor and the subsequent dissociation of silicon nitride to silicon and nitrogen are, together, much faster than the traditional carbothermal process for the production of silicon, which typically takes a day or longer, and a subsequent ~~pöcess~~process to purify the carbothermal silicon. This is also because the last bits of residual phosphorous can be removed from the silicon nitride product by treatment with sodium hydroxide. Thus, because the resulting silicon nitride is extremely pure, having very low levels of phosphorous, the silicon from disassociation of silicon nitride is extremely pure. On the other hand, if the silicon was produced directly in a carbothermal step, the residual phosphorus would become trapped in the molten silicon and after solidification of the silicon, it would be impossible to remove this small amount of residual phosphorous

#### PRIOR ART

35. I have read and am generally familiar with the Office Action mailed October 30, 2008 that rejects claims 106-160 of the '924 application under 35 U.S.C. §103(a) as being unpatentable over U.S. 4,591,492 to Tanaka, et al. ("Tanaka") and, independently, as being unpatentable over U.S. 6,117,810 to Lee et al. ("Lee"). I have also read and am generally familiar with the Tanaka and Lee patents. For reasons stated below, I respectfully disagree with Examiner's conclusions regarding the alleged obviousness of my claimed inventions.

U.S. 4,591,492 to Tanaka, et al.

#### A. Products of Interest.

36. Tanaka only discloses a method for making silicon carbide ~~only~~, although Tanaka mentions that U.S. 4,525,335 illustrates the formation of silicon nitride whisker crystals (Col. 11, lines 32-45). In contrast, the subject application claims (1) carbon-silica products (above, "Leached Product"); (2) devolatilized carbon-silica products

(above, "~~Devolatilized~~Devolatilized Leach Product"); (3) silicon carbide; (4) silicon nitride and (5) silicon.

37. Tanaka makes no composition of matter claims on silicon carbide or any other intermediate products such as the product of the ~~leach~~leaching operation. Moreover, ~~Tanka~~Tanaka fails to disclose the effect of leaching on the carbon : ~~silica or carbon : silicon~~ mole ratios of the leach product or any other products. In contrast, we make composition of matter claims on all of the above mentioned products and disclose detailed information on the effects of the leaching operation on the carbon : silica mole ratio of the leach products.

38. Although Tanaka mentions the carbon : silicon ratio of the rice hulls used, it makes no mention of the carbon : silicon ratios of the leach product or any other intermediate product. The carbon : silicon ratios stated in Tanaka for the rice hulls are from "7:3 to 5:5" (Column 3). These are the same as 2.33:1 and 1:1. The Tanaka values are not even close to the value of about 4:1 that is consistently given in the literature. Thus, Tanaka's ability to measure even the carbon : silica mole ratio of the rice hulls is called into question. Moreover, these ratios are well below the desired ratio of about 3:1 for silicon carbide production and it is hard to imagine how his leaching process could increase the ratio from the low values he gives for rice hulls to higher values in the leached product.

39. It is not obvious from Tanaka what the effect of hydrochloric acid is on the carbon : silica mole ratio in the leach product, let alone what the effect of sulfuric acid would have on the carbon : silica mole ratio in the leach product or any other intermediate product.

#### B. Type of acid.

40. Tanaka discloses the use of hydrochloric acid, nitric acid and sulfuric acid. In contrast, to the extent that our claims recite an acid, they recite only sulfuric acid.

41. The information and discussion in Tanaka are focused on hydrochloric acid. Tanaka contains no evidence about the use or affects of acids other than hydrochloric acid with or on rice hulls. Tanaka does not provide any rationale or teaching for why other acids might provide desired results. It is well know that different acids have different effects on biomass and there is no reason to expect, *a priori*, that the results achieved with one acid such a hydrochloric acid will be duplicated or even close with another acid. For example, cellulose is a major component of rice hulls and it is well known that sulfuric acid hydrolyzes cellulose to the individual glucose molecules that make up cellulose. On the other hand, nitric acid is an oxidizing agent and its effect on cellulose and other components of biomass is different ~~than~~from that of sulfuric acid.

42. It is therefore not obvious from ~~the Tanaka Patent~~ what the ~~affects~~effects of sulfuric acid will be on rice hulls.

#### C. Acid Concentration.

43. Tanaka discloses a method of manufacturing silicon carbide crystals in which a rice husk raw material is treated with an acid solution (e.g. 5N to 6 N  $H_2SO_4$ , or HCl or  $HNO_3$ ) prior to being heated in a furnace of non-oxidizing atmosphere. Tanaka expresses the recommended acid concentrations in terms of normality—5-6 N. In the text, Tanaka also states that concentrated ~~HCL~~HCl is 12 normal, but it doesn't tell the reader that 12 normal HCl is actually only 37 % ~~HCL~~HCl. Thus, the reader has to know what the actual concentration of 12 N ~~HCL~~HCl is before he can determine the actual wt % of ~~HCL~~HCl in the leach solution. By assuming that concentrated HCl is 37% ~~HCL~~HCl, we calculate the ~~HCL~~HCl concentrations of 5-6 N solutions to be 15% to 19% ~~HCL~~HCl, which, to us, seems like a high concentration of ~~HCL~~HCl.

44. Turning now to sulfuric acid, Tanaka presents no evidence regarding the effect of sulfuric acid on rice hulls, but suggests that the same concentrations of acid used for HCl (5-6N) will work optimally for  $H_2SO_4$ . Tanaka states that concentrated sulfuric acid is 36 N, and the reader must know that such acid contains 98% sulfuric

acid, and then carry out a calculation to try to figure out the ~~actual~~actual concentration of sulfuric acid to which Tanaka is referring. We calculate that 5-6 N H<sub>2</sub>SO<sub>4</sub> corresponds to an acid concentration of 14-16 wt %. This is a very high acid concentration that is well above the optimum concentration (1-2.5wt %) recommended in our application. In this regard, we have evidence that sulfuric acid concentrations above about 5% results in leach products that contain significantly more phosphorous.

45. Tanaka fails to teach the importance of acid concentration and does not disclose the use of sulfuric acid concentrations as claimed in our application. Moreover, Tanaka teaches that excessive dilution of the acid with water will lessen its effectiveness.

46. We also have evidence indicating that sulfuric acid, at the concentrations of hydrochloric acid used by Tanaka, provides less than desirable results. It is not obvious from Tanaka what affects lower, more cost- effective concentrations of hydrochloric acid will have on the leach product and it is certainly not obvious from Tanaka what effects the concentration of sulfuric acid claimed will have on the leach product.

#### D. Rice Hull Concentration.

47. At Column 3, Tanaka states that the amount of acid utilized in the pretreatment step is preferably 10 to 40 liters per kilogram of rice husks (approximately 10 to 40 weight percent, based on the weight of the husks), optimally 20-30 liters/Kg. (approximately to 30 percent). ~~The~~Tanaka says the 20 to 30 liter range is particularly appropriate in instances where the mixture of rice husks is agitated during the treatment process.

48. A liter of acid weighs about 1 Kg. Thus, 10 liters of acid mixed with 1 Kg of rice husks ~~gives~~produces a ~~solution~~slurry that is about 10% ~~based on the weight of the~~ wt% rice husks. However 40 liters of acid mixed with 1 Kg of rice husks results in a ~~solution~~slurry that is about 3% ~~based on the weight of the~~ rice husks as opposed to the



40% indicated by Tanaka. Thus, Tanaka provides information that is inconsistent and confusing with regard to the rice hull concentration he actually used. ~~Thus, and~~ the reader does not know what rice hull concentrations he actually used.

49. Tanaka fails to disclose teachings regarding what the desirable concentration of rice hulls is in the leaching process with sulfuric acid. In contrast, we clearly ~~describes~~describe the actual rice hull concentration used in all examples of the leaching process and in discussions of the leaching process.

~~DE~~. Temperature.

50. Tanaka discloses "boiling". However, the temperature of "boiling" is highly dependent on the location and on the type and concentration of acid. Thus the actual temperature that Tanaka discloses is unknown. In contrast, we disclose a range of leaching temperatures from 10 deg C to 250 deg C and provide detailed information on the different effects of different temperatures.

51. It is not obvious from Tanaka how temperature affects the properties of the leach product produced with hydrochloric acid, and it is certainly not obvious from Tanaka what effect the leaching temperature would have on the properties and purity of the ~~leach product~~Leach Product produced with sulfuric acid.

52. In Column 3, Tanaka states that although the application of heat or agitation will lessen the pretreatment time, boiling is most effective. Use of the word "boiling" does not tell the reader what the temperature actually was. The boiling point of a solution of HCl is highly dependent upon the concentration of ~~HCL~~HCl, the altitude where the treatment takes place and the concentration of rice hulls. At sea level, a 10% solution of HCl boils at about 103 deg C, whereas a 20% solution of ~~HCL~~HCl boils at 108 deg C, whereas a 38% solution of ~~HCL~~HCl boils at 48 deg C. If ~~Tanka~~Tanaka's ~~HCL~~HCl solutions are 5-6 N, the boiling point at sea level is about 103 deg C to 108 deg C. However, even with some knowledge of the effect of the concentration of HCL on the

boiling point of HCL solution at sea level, one does not know Tanaka's actual temperature.

53. We have found that relatively small changes in temperatures around ~~94 deg C~~ between "boiling" and 120 deg C can have a significant effect on the concentration of ~~phosphorouselements~~ such as phosphorus and iron in the leached product. Because this biomass system and process involve both organic and inorganic components, significant changes can and do occur during acid leaching that likely would not be apparent to one accustomed to working primarily with organic components.

54. Tanaka's imprecise definition of temperature does not allow the reader to make any real correlation between the actual temperature and the effects described by Tanaka. Furthermore, the boiling point of water at sea level is about 100 deg C, but in Golden, Colorado where we have done our work, the boiling point of water is about 96 deg C. Thus without telling the reader the altitude connected to his "boiling point," one is even more confused about what the actual temperature was.

#### EE. Time.

55. ~~54. The Tanaka patent discloses only two times: boiling for a period of 0.5 hours and to one hour, or preferably 2 hours (Col. 13, lines 1-3).~~ In contrast, we disclose and recite in our claims a range of times from six seconds to 48 hours, and provide descriptions of the effects of different leaching times. It is not obvious from Tanaka how different leaching times affect the leach product of the hydrochloric leach operation. No trends are shown. Thus one would be forced to carry out a complete analysis of the effect of time on the product of the leach process even if hydrochloric acid were used. Clearly, with respect to the use of sulfuric acid, it is not obvious from Tanaka what the effect of time has on the leach product.

U.S. 6,117,810 to Lee, et al.

56.     ~~55.~~ I believe Lee is unrelated to the subject application. The products are not the same. The raw materials are not the same. The processes for converting the raw material into the product are completely different.

57.     ~~56.~~ The product of interest in Lee is a molecular sieve compound made of carbon and aluminosilicate. The products of interest in our application are (1) carbon-silica products (above, "Leached Product"); (2) devolatilized carbon-silica products (above, "~~Deolvatilized~~Devolatilized Leach Product"); (3) silicon carbide; (4) silicon nitride and (5) silicon.

58.     ~~57.~~ The raw materials used in Lee are activated carbon, various aluminum containing materials, and colloidal silica or fumed silica or water glass or silica gel. The raw materials used in our application are rice hulls, rice straw and other plant materials containing at least 1% silica.

59.     ~~58.~~ The Lee process involves forming an aluminum silicate gel and then embedding the gel in the pores of the activated carbon. The leaching step of our process involves treating rice hulls, rice straw and other plant matter containing at least 1% silica with various concentrations of sulfuric acid at various temperatures and for various times to produce carbon silica products with mineral concentrations much lower than the concentrations in rice hulls, and with carbon : silica mole ratios optimal for the production of the Devolatilized Leach Product, silicon, silicon carbide, silicon nitride and silicon tetrachloride, and with much higher porosity than rice hulls.

60.     ~~59.~~ All testing referred to in paragraphs 7-8, 12-17 and part of the testing mentioned in paragraph 18 above were done prior to filing the subject application. Part of the testing mentioned in paragraph 18 above and all of the testing referred to in paragraphs 19, 22 and 24-34 were done after the filing of the subject application.

61.     ~~60.~~ I believe that an invention embodying the elements recited in combination in each respective pending claim as amended in the Amendment and Response filed concurrently with this Declaration have not been disclosed in any prior

art reference of which I am aware. I further believe that the invention as recited in each claim presented in the application as amended in the Response filed concurrently with this Declaration would not have been obvious to a person of ordinary skill in the art having knowledge of the prior art at the time my disclosures of the claimed subject matter were made in the '924 application.

62. ~~61.~~ All statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true. To the extent that any statement made herein differs, or can be read or interpreted to differ, from any statement made in my Declaration previously made in connection with the prosecution of United States Patent Application No. 10/822,924 on April 29, 2009 ("Prior Declaration"), any and all such differences are based upon more careful reading of the Prior Declaration and/or the cited prior art references and/or error inadvertently made during preparation of the Prior Declaration, all of which were made in good faith and without any intent to deceive the Examiner, the United States Patent and Trademark Office, or any other person who may later have reason to read or consider my statements made in the Prior Declaration or herein.

I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. §1001), and may jeopardize the validity of the application or any patent issuing thereon.

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Norman D. Hinman

Date: ~~April 30,~~ June 29, 2009

Document comparison by Workshare Professional on Monday, June 29, 2009 4:34:44 PM

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Insertions	67
Deletions	64
Moved from	2
Moved to	2
Style change	0
Format changed	0
Total changes	135